

## Synthesis and characterization of copper substituted tungsto heteropoly salt

K. C. DEY<sup>1\*</sup> and V. SHARMA<sup>2</sup>

<sup>1</sup>Department of Chemistry, Jamshedpur Cooperative College,  
Jamshedpur, Ranchi University, Ranchi (India)

<sup>2</sup>Department of Chemistry, RVS College of Engg and Technology,  
Jamshedpur, Ranchi University, Ranchi (India)

(Received: April 12, 2008; Accepted: June 04, 2008)

### ABSTRACT

A mixed heteropoly compound with molecular formula as  $\text{Na}_{13}[\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}\text{W}^{\text{VI}}\text{O}_{24}]\cdot 16\text{H}_2\text{O}$  analogous to the type  $[\text{X}^{\text{n}}\text{M}_5\text{O}_{24}]^{(12-\text{n})}$  has been synthesized from an aqueous acidic solution containing sodium tungstate, copper chloride and ferric chloride. The complex anion has two heteroatoms, thus a mixed addenda compound. This substituted heteropoly compound is characterized by elemental analyses, IR studies, thermal analysis, molar conductance and molecular weight determination.

**Key words:** Heteropoly compound.

### INTRODUCTION

A wide range of polyoxometalates (POMs) is formed with frame works built from transition metal ions linked by bridging oxide ions. POMs are multi functional materials and have been widely used in analytical and clinical chemistry, catalysis [including photo-catalysis], biochemistry [electron transport inhibitors] medicine [anti-tumoral<sup>1-4</sup>, anti-viral and even anti-HIV activity] and solid state devices<sup>5</sup> due to their unique combination of physical and chemical properties. POMs as inorganic – organic hybrid materials have received increasing attention over last few years for their specific properties<sup>6-8</sup>. The mechanism of formation of POMs is difficult to understand because even very large structures can be synthesized in one pot condensation reaction in aqueous acidic medium by interaction of the composing elements with the need of any polyoxoanion precursor species<sup>9</sup>. e.g.  $[\text{As}_{12}\text{Ce}_{16}\text{H}_2\text{O}_{36}\text{W}_{148}\text{O}_{524}]^{1-76}$ . Heteropoly acids are currently of great interest due to particularly their nanosized structures and their potential application<sup>10-11</sup>. In the later part of 20<sup>th</sup> century and beginning of 21<sup>st</sup>

century<sup>12</sup> heteropoly oxometalates have found more attention because they are low in toxicity, highly stable towards humidity, recyclable and are air stable<sup>13</sup>. Thus the use of heteropoly acids (HPAs), their salts and polyoxometalates (POMs) as industrial catalysts is ecofriendly and green which reduces or eliminates the use or generation of hazardous substance throughout the entire life of chemical materials.

The first Copper containing derivative of Tungsto-arsenate (III) was structurally characterized in 1982<sup>14</sup>. Siedle reported the EPR properties of Sodium salts and the mixed Sodium Potassium salt of Copper (II) substituted heteroanion<sup>15</sup>. The maintenance of the acidic medium in suitable pH range for the preparation of heteropoly anion is an essential condition<sup>16</sup>. In the present communication, we report the synthesis and Characterization of Copper substituted Tungsto iron heteropoly salt by elemental analyses, IR studies, thermal analysis, molar conductance and molecular weight determination.

## MATERIAL AND METHODS

### Following reagents were used for the synthesis of heteropoly oxometalate

- Copper Chloride dihydrate. [BDH make]
- Sodium Tungstate dihydrate [BDH make]
- Ferric Chloride [E. Merck] 99.5% purity
- Glacial Acetic Acid [BDH make]
- Acidic Buffer tablet of pH=4 [Qualigens]

All the above reagents were of analytical grade and their solutions were prepared freshly by dissolving the requisite amount of reagents in distilled water. The pH of the solution was recorded by El digital pH meter model 111E and the conductivity was noted from El Digital Conductivity meter model 611. The copper, iron, tungsten and sodium metal present in the compound were estimated by using Inductively coupled plasma atomic emission spectroscopy, (make Jobin Yvon France of model JY Ultima -2) at IIT Powai, . The IR spectra were recorded by Perkin Elmer 577 spectrophotometer in the region 4400-450  $\text{cm}^{-1}$ . The thermal experiments were carried out by heating the compound from 42°C-650°C at 10°C/min using Perker Elmer USA of model Diamond TG-DTA. The molecular weight was determined by cryoscopic method using Beckmann's thermometer.

### Synthesis of Tungsto iron cuprate(II) oxometalate

1.05g (6 mmol) analyzed copper chloride was dissolved in 30ml distilled water which was mixed with 30ml solution containing 1g (6 mmol) ferric chloride. 10ml of glacial acetic acid was added to it<sup>17-18</sup>. This mixture was added drop wise with constant stirring to the sodium tungstate solution prepared by dissolving 10.17g (31mmol) in 75 ml of the distilled water. After each addition, the pH and the conductivity of the resultant solution were noted. After the addition of 57ml of mixture solution to sodium tungstate solution, the pH and the conductivity of the resulting mixture became constant at 3.9 and 18.2  $\Omega^{-1}$  respectively. An acidic buffer tablet of pH=4 was dropped into the reaction mixture. The mixture was refluxed for 3hrs. It was filtered and filtrate was left for crystallization<sup>19-23</sup> at 5°C. 2.54gm of amorphous light blue small crystals were separated out which were washed with n-hexane and preserved for analysis.

## RESULTS AND DISCUSSION

When the theoretical quantities of the reagents, on the basis of probable Anderson structure of heteropoly complex ion  $[X^{n+}M_6O_{24}]^{-(12-n)}$  are refluxed under pH=4, the crystals of  $Na_{13}[Cu^{II}-Fe^{III}W^VI_5O_{24}].16H_2O$  are separated out. The complex is non-hygroscopic, crystalline in nature, stable at room temp and soluble in water. The observed elemental analyses data of the compound as recorded from ICPAES results are found as Na, 14.92; Cu, 3.1; Fe, 2.77; W, 46.28; O, 18.77% (by diff). Calc. [Na, 14.91; Cu, 3.1; Fe, 2.73; W, 46.12; O, 18.74% (by diff)]. On the basis of the percentage composition of different metals present in the compound and the number of water molecules as calculated from the TGA data, the molecular formula of the compound is formulated as given above. The results have been corroborated by standard chemical methods.

The IR spectra of this new synthesized mixed heteropoly complex show characteristics band positions, shifts and intensities in comparison with the polytungstates<sup>24</sup> complex which can be correlated to mixed heteropoly oxometalates. The compound shows sharp peaks at 1144 - 1651  $\text{cm}^{-1}$  which may be assigned to independent W-O stretching vibration and the broad band at 768-798  $\text{cm}^{-1}$  may be due to W-O-W bridge vibration. The sharp band at 834-932  $\text{cm}^{-1}$  may be attributed to Fe-O linkage. The medium band in the region of 501-573  $\text{cm}^{-1}$  reveals the presence of Cu-O bond in the octahedral complex. Besides these, bending of water molecules is also evident from IR spectra. The broad band of lattice water is observed at 1730  $\text{cm}^{-1}$ .  $FeO_6$  and  $CuO_6$  octahedra act as hetero group which replace two octahedra from  $[X^{n+}M_6O_{24}]^{-(12-n)}$ . The thermal decomposition is completed in two steps due to dehydration of crystals water. The residual amount of the first step is 90% from 96°C to 182°C and that of the second step is 73% from 182°C to 310°C. Finally, the insoluble oxides are given as the last product. The higher value of conductance of this copper (II) complex indicates the electrolytic nature of the compound. The apparent molecular weight of the compound has been found 1939.85 as determined by cryoscopic method using  $Na_2SO_4.10H_2O$ -water system as solvent<sup>25</sup> against calculated molecular weight of 2041.85.

**ACKNOWLEDGEMENTS**

The authors are thankful to the SAIF, IIT Powai for the result of elemental analyses. One of

the authors (V.Sharma) is thankful to the Director RVSCET, JSR for providing the resources for the synthetic work.

**REFERENCES**

1. Pope M.T. and Muller A., *Angew Chem., Int.Ed. Engl.*, **30**: 34-48(1991).
2. Hill C.L, Prosser-Mc, and Cartha C.M., *Coord. Chem. Rev.*, 407-455(1995).
3. Hill C.L. Polyoxometalates in catalysis, Ed J of Molecular catalysis Amsterdam, 114, (1996).
4. Newmann R., *Prog. Inorg. Chem.*, **47**: 317-370 (1998)
5. Coronado E. and Gomez-Garcia C.J, *Chem. Rev.*, **98**: 273 (1998).
6. Mayer C.R., Cabuil V., Lalot T. and Thouenot R., *Angew. Chem. Int.*, Ed.**38**: 3672 (1999).
7. Stanger U.L., Groseij N., Orel B., Schmitz A. and Colomban P., *Solid state ionics*, **145**: 109 (2001).
8. Zhang T.Y, Feng W., Lu R., Zhang X.T., Jin M., Li T.J., Zhao Y.Y. and Yao J.N., *Thin solid Films*, **402**: 273 (2002).
9. Wassermann K, Dickman M.H and Pope M.T, *Angew Chem.*, 109 (1997).
10. Zacharie B., Connolly T.P, Attardo R. and Penney G., *Tetrahedron*, **52**: 2271 (1996).
11. Anderson J.D., Cotton H.B., Larson S.B., Noed L.D, Revankar G.R. and Robins R.K., *J. Heterocycl. Chem.*, **27**: 439 (1990).
12. Ulrich K., Masha.Savetieff G., Bassem S.B., Bineta K.and Louis N, *Inorg.Chem*, **41**: 783-789 (2002).
13. Mullar A. and Roy S., *Coord. Chem. Rev.*, **14**: 153- 245 (2003).
14. Robert, Leyrie M. and Herve G., *Acta Crystallogr.*, B-**38**: 358 (1982).
15. Siedle A.R. and Goldstein C., *J. of. Am. Chem. Soc.*, **105**: 7447 (1983).
16. Gimblett F.G.R., *Inorganic Polymer Chemistry*, Butterwoods, London, 8 (1963).
17. Kelpert D.L, The early transition elements, Acad.press, New Delhi., **46-60**: 288-304 (1972).
18. Roy S.K. and Dey K.C., *Indian. J. Chem.*, **31A**: 64-66 (1992).
19. Mellor J.W, "A Comprehensive Treaties on Inorganic and Theoretical chemistry". London, Vol-X and XI, Longman Green and Co., (1931)
20. Baker L.C.W., Lov B.and Mc Cutcheon T.P., *J.Ame.Chem.Soc.*, **72**: 2378 (1950).
21. Brawer G. (Ed) "Hand Book of preparative Inorganic Chemistry", 2nd edit, New York, Academic press, Inc., **2**: 1698 (1965).
22. Pope M.T.and Popaconstantinaus E., *Inorg. Chem.*, **5**: 1249-1740 (1966).
23. Bhattacharya G.C. and Roy S.K., *J. Indian. Chem Soc*, 50: 356 (1973).
24. Weakly J.R, *Structure and Bonding*, **18**: 153 (1974).
25. Flynn C.M.and.Pope M.T., *Inorg. Chem.*, **10**: 25- 26(1971).